(12) UK Patent Application (19) GB (11) 2 171 718 A

(43) Application published 3 Sept 1986

(21) Application No 8603630

(22) Date of filing 14 Feb 1986

(30) Priority data
(31) 8502339 (32) 15 Feb 1985 (33) FR

(51) INT CL[4]
C07C 1/20

(52) Domestic classification (Edition H):
C5E 321 386 392 CF

(56) Documents cited
EP 0054805 EP 0054375 EP 0023303

(58) Field of search
C5E
Selected US specifications from IPC sub-class C07C

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(54) Olefin preparation

(57) The invention concerns a process for converting methanol or dimethyl ether to olefins in the presence of a dealuminated mordenite, wherein the reactant (methanol or dimetyl ether) is diluted with a gas or with steam.

It is characterised in that the obtained olefins are fractionated so as to recycle at least a part of the olefins having at least 4 carbon atoms per molecule.

The invention is particularly applicable to the production of propylene.

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SPECIFICATION

Olefin preparation

The invention relates to a process for manufacturing olefins, in particular, propylene with the simultaneous formation of a minor proportion of butenes, by converting methanol and/or dimethyl ether in the presence of certain aluminosilicates.

The conversion of methanol to hydrocarbons is a long known but remarkable reaction during which carbon-carbon bonds are formed from C_1 "radicals" formed from the methanol in the presence of certain acid catalysts. However this conversion has only recently become of industrial importance due to

–the discovery of sufficiently active, and particularly selective catalysts capable of converting methanol to hydrocarbons and particularly to motor gasoline hydrocarbons, and

–the policies of oil-producing countries which resulted in disruption of economical and technical aspects of the petrochemical and oil industries.

Methanol is generally obtained from natural gas, but it may also be obtained from heavier hydrocarbons by fermentation, by distillation of wood etc... and from coal or from any other material of high content of carbon derivatives.

The conversion of methanol to hydrocarbons, may form a source for synthesized motor fuels. Economically, the production of hydrocarbons from methanol seems to be more competitive than techniques for synthesizing motor fuels from coal.

By suitable selection of catalyst and by adaptation of operating conditions, it is possible to adjust the conversion of the methanol to the production of light or heavier hydrocarbons, as well as of aromatic compounds or olefins.

The present invention is particularly concerned with a process for manufacturing propylene from methanol or dimethyl ether or a mixture thereof, said process being of high interest in the present economical conditions.

Propylene is one of the best known starting materials for the chemical and petrochemical industry and is an important light olefin. For example, it is widely used for manufacturing alkylates and polymerization gasolines to improve the octane number of motor fuels.

It has also been used in very substantial amounts for manufacturing plastic materials such as polypropylene and also for manufacturing other products such as: acrylonitrile, propylene oxide, propanol and cumene.

Up to now, propylene has been mainly obtained as a product of oil refining and generally by steam-cracking naphthas. However, oil refining operations now tend towards steam-cracking of heavier products, instead of "naphtha" cuts, thus decreasing propylene production.

Catalysts hitherto used for the conversion of methanol to hydrocarbons generally include zeolites or contain zeolites which are crystallized alumino-silicates and are convenient for this conversion apparently because of their acidic properties, and

–as a result of their well-defined crystal structure, the size of their interstices being of the same order of magnitude as the size of the organic molecules therein during the reaction.

The major disadvantage of this methanol conversion method is the rapid deactivation of the catalyst due to irreversible deposits of very condensed organic products ("coke").

Many attempts to solve this problem have been reported in the technical literature. These generally involve the modification, by various means, of the catalytic properties of the alumino-silicates in order to give them higher selectivity and hence to decrease "coke" formation on their surface.

European Patent No. 0084 748 discloses a process for selectively producing olefins from methanol or dimethyl ether using a catalyst optimized for the production of light olefins. In particular, this discloses the use, for producing C_{2-5} unsaturated hydrocarbons, of a catalyst consisting mainly of zeolite modified so as to very considerably increase its life-time and selectivity. Modification consists in dealuminating a zeolite of the synthetic mordenite type. The modified zeolite, in order to have a good selectivity for olefin production, must have a Si/Al atomic ratio of from 80 to 150. We have now found that by proceeding under specific operating conditions it is possible to noticeably improve propylene yields.

According to the invention there is provided a process for the manufacture of C_{2-5} olefins from a reactant comprising methanol, dimethyl ether or a mixture thereof, effected in the presence of at least one catalyst comprising dealuminated mordenite with a Si/Al atomic ratio higher than 80; a Na_2O content lower than 0.1% by weight; a specific surface, after shaping, of from 390 to 600 m^2/g; a total pore volume of from 0.540 to 0.650 cm^3/g; and a pore volume for pores of a diameter greater than 10 nm of from 0.350 to 0.550 cm^3/g; wherein the reactant is diluted with a carrier gas or steam, the concentration of the reactant in the carrier gas or steam fed to the reaction zone being from 5 to 75% by volume, the hourly volume flow rate being from 0.5 to 100 litres of liquid reactant per litre of catalyst per hour, the temperature being from 300 to 650°C and the pressure from 0.01 to 3 MPa; and wherein after separation of olefins from the

reactant and from the reactant diluent (gas or steam), the olefins are fractionated so as to recover, a cut comprising C_{2-3} hydrocarbons, and a cut containing, as a major part, higher olefins having a least 4 carbon atoms per molecule, the higher olefin cut being at least partly recycled to the reaction zone.

We have found that the best yields of olefins having 2 to 5 and preferably 3 to 4 carbon atoms per molecule are obtained by reacting, in the presence of a dealuminated zeolite, methanol and/or dimethyl ether at a sufficient temperature and by sufficiently diluting the reactant with at least one gas (e.g. nitrogen, hydrogen, carbon monoxide, carbon dioxide) or steam.

In practice, the reactant (methanol and/or dimethyl ether), diluted with the carrying gas or with steam, is reacted over at least one catalyst of the dealuminated mordenite type, at a pressure ranging from 0.01 to 3 MPa and preferably from 0.1 to 0.5 MPa and at a temperature ranging from 300°C to 650°C, preferably from 350°C to 550°C.

The reactant concentration in the gas (or steam) passing over the catalyst bed will range from 5 to 75% by volume, preferably from 25 to 60%.

The hourly volume flow rate or liquid hourly space velocity (LHSV) will range from 0.5 to 100 litres of liquid methanol per litre of catalyst per hour, preferably from 0.5 to 50 litres.

The products from the reaction zone are conveniently conveyed to a separation zone wherefrom the olefins are separated from unreacted reactant (methanol and/or dimethyl ether), which is at least partly recycled, and from the one or more reactant diluents (gas or steam) which may also be recycled. The hydrocarbons obtained are then subjected to separation in order to recover a cut of high C_{2-3} olefinic hydrocarbons content, and a cut containing a major part of higher olefins having at least 4 carbon atoms per molecule, said cut generally containing also butanes.

It has been observed that when recycling at least a part of the higher olefins cut to the reactor input where it is contacted with the catalyst jointly with the methanol and/or dimethyl ether, two advantages are obtained:

(a) a part of the heat produced by the reaction is removed, and
(b) the yield of propylene and the catalyst life-time are noticeably increased.

Preferably 20 to 60% by weight of the higher olefins cut is recycled.

The catalyst may be arranged in two or more successive beds, in one or more reactors. This arrangement has the advantage to make easier the removal of heat evolved during the reaction. The catalyst may be in a fixed bed arrangement. The catalysts may also be used in a moving bed contained in one or more moving bed reactors, said technique providing for an easier removal of the heat evolved during the reaction and having also the advantage of increasing the space velocity of the reactants with an improvement in selectivity. In this arrangement the charge successively flows through each reactor or reaction zone in axial or radial flow (radial meaning a flow from the center towards the periphery or from the periphery towards the center). The reaction zones may be arranged in series, for example side-by-side or superposed. The charge successively flows through each of the reaction zones, if desired with introduction of charge or of intermediary recycle between the reaction zones in order to control the temperature of the reaction by addition or removal of heat; fresh catalyst may be introduced at the top of the first reaction zone with the fresh charge, then it flows progressively downwardly through said zone, wherefrom it may be progressively withdrawn at the bottom, and, by any convenient means (particularly a lift for reactors placed side-by-side), it may be conveyed to the top of the next reaction zone where-through it progressively flows also downwardly, and so on, up to the last reaction zone, at the bottom of which the catalyst may be progressively withdrawn and then fed to a regeneration zone. From the output of the regeneration zone the catalyst may be progressively reintroduced at the top of the first reaction zone. The various catalyst withdrawals are conveniently effected progressively, as above-mentioned, i.e. either periodically or continuously. Continuous withdrawal is preferred to periodical withdrawal.

The catalyst used according to this invention may be prepared and has the same performance as disclosed in European Patent No. 0084748. It comprises a dealuminated mordenite in which the Si/Al atomic ratio is higher than 80, preferably from 80 to 96 and more particularly from 87 to 90, with a Na_2O content lower than 0.1% by weight. The specific surface, after shaping, with an optional addition of about 5 to 40%, for example 10%, by weight, of a clay binding agent, ranges from 390 to 600 m^2/g and preferably from 420 to 550 m^2/g, and the total pore volume ranges from 0.540 to 0.650 cm^3/g and preferably from 0.550 to 0.600 cm^3/g. The pore volume, for pores of diameter greater than 10 nm ranges from 0.350 cm^3/g to 0.550 cm^3/g and preferably from 0.400 to 0.500 cm^3/g, and its bed density for pellets of about 3×2 mm, ranges preferably from 0.600 to 0.700 g/cc.

The following Examples serve to illustrate the invention. The catalyst used in the Examples comprises, as major constituent, a pelletized (3×2 mm) dealuminated mordenite with the following characteristics:

Surface	450 m^2/g
Total pore volume	595 cm^3/g
Pore volume for pores > 10 nm	0.460 cm^3/g
Bed density (packed) (for 3×2 mm pellets)	0.650 g/cm^3
Si/Al atomic ratio	89.2

The charge was a 50/50 mixture by weight of water and methanol. The reaction was conducted in a pilot unit having a straight vertical reactor containing 40 cm^3 (26 g) of pelletized catalyst (3×2 mm) including 10% of clay binder (specific surface of the catalyst mass of 455 m^2/g).

The catalyst is brought to a temperature of 500°C with an air flow of 250 l/h, previously dried by passage through an alumina bed for 2 hours.

After this pretreatment, the 50/50 by weight mixture of methanol with steam is passed through the catalyst bed.

The operating conditions, which are the same in all the following examples, are:

Pressure	atmospheric
Temperature	460°C
LHSV	1 h^{-1} (litre/h)

The test is considered as completed when the sum of produced C_2,C_3 and C_4 olefins becomes smaller than 10% by weight of the initial yield. This time is about 50 hours.

EXAMPLES

In the following examples the whole unconverted methanol amount and the whole steam amount were recycled.

Example 1

This test was conducted for 50 hours under the above-mentioned conditions without recycling of the C_{4+} hydrocarbons (charge : 50% by weight water, 50% by weight methanol).

Example 2

This example was conducted in the same operating conditions as in Example 1 but with a recycling of at least a portion of the obtained C_{4+} hydrocarbons.

The charge composition here including the recycle, was then as follows:

Water	50% by weight
Methanol	42.5% by weight
C_{4+} recycle	7.5% by weight

At the reactor output and after separation of steam and of unreacted alcohol, the hydrocarbon effluent is fed to a distillation zone wherefrom are separated, from the column bottom, the C_{4+} hydrocarbons, amounting to 12.51% by weight of the total charge fed to the reaction zone (water, alcohol and hydrocarbons) and having, by weight, the following composition:

Butanes	15.10
Butenes	63.15
C_{5+}	18.15
Aromatics	3.60

At the top of the fractionation zone are withdrawn the C_1, C_2, and C_3 hydrocarbons containing more than 90% by weight of propylene.

The composition by weight of this cut of very high propylene content is as follows:

Methane	1.28%
Ethane	0.16%
Ethylene	5.13%
Propane	1.20%
Propylene	92.23%
	100.00%

The cut containing the C_{4+} hydrocarbons amounts to 12.51% by weight of the total amount of

products fed to the reaction zone; 59.95% by weight of this cut are recycled to the reaction zone, this recycle amounting to 7.5% by weight of the total charge fed to said zone.

The remainder of said cut (i.e. 40.05%) is fed for example to a gasoline pool.

The following Table sets out the percentage composition by weight of the products obtained in Examples 1 and 2 in proportion to the charge (after 50 hours of treatment).

TABLE I

	EXAMPLE 1	EXAMPLE 2
	Products	Products
Methanol	2.73	2.34
Dimethyl ether	0.19	0.16
Water	76.50	72.52
C_1 to C_3 paraffinic hydrocarbons	0.33	0.33
Ethylene	0.66	0.64
Propylene	12.09	11.50
C_4 +	7.50	12.51

From the obtained results as reported in the above Table, it is observed that, when operating in the conditions of Example 1, i.e. without recycling the obtained C_4 hydrocarbons, propylene production amounts to 25.57 kg for 100 kg of converted methanol, whereas when recycling said hydrocarbon cut 28.63 kg of propylene are obtained for 100 kg of converted methanol.

CLAIMS

1. A process for the manufacture of C_{2-5} olefins from a reactant comprising methanol, dimethyl ether or a mixture thereof, effected in the presence of at least one catalyst comprising dealuminated mordenite with a Si/Al atomic ratio higher than 80; a Na_2O content lower than 0.1% by weight; a specific surface, after shaping, of from 390 to 600 m^2/g; a total pore volume of from 0.540 to 0.650 cm^3/g; and a pore volume for pores of a diameter greater than 10 nm of from 0.350 to 0.550 cm^3/g; wherein the reactant is diluted with a carrier gas or steam, the concentration of the reactant in the carrier gas or steam fed to the reaction zone being from 5 to 75% by volume, the hourly volume flow rate being from 0.5 to 100 litres of liquid reactant per litre of catalyst per hour, the temperature being from 300 to 650°C and the pressure from 0.01 to 3 MPa; and wherein after separation of olefins from the reactant and from the reactant diluent (gas or steam), the olefins are fractionated so as to recover, a cut comprising C_{2-3} hydrocarbons, and a cut containing, as a major part, higher olefins having a least 4 carbon atoms per molecule, the higher olefin cut being at least partly recycled to the reaction zone.

2. A process according to claim 1, wherein 5 to 40% by weight of clay type binder are added to the dealuminated mordenite.

3. A process according to either of claims 1 and 2, wherein the Si/Al atomic ratio of the dealuminated mordenite is from 80 to 95.

4. A process according to any one of the preceding claims wherein the pore volume, for pores of diameter larger than 10 nm, is from 0.400 to 0.500 cm^3/g.

5. A process according to any one of the preceding claims, wherein 20 to 60% by weight of the higher olefins cut is recycled.

6. A process according to any one of the preceding claims for producing propylene in a

major proportion.

7. A process according to any one of the preceding claims wherein at least one part of the unreacted reactant and at least one part of the gas or steam used to dilute said reactant are recycled.

8. A process according to any one of the preceding claims substantially as herein described.

9. Propylene whenever produced by a process as claimed in any one of the preceding claims.

10. Each any every novel process, product, apparatus and method as herein disclosed.

Printed in the United Kingdom for Her Majesty's Stationery Office, Dd 8818935, 1986, 4235.
Published at The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.